Dimolybdenum Complexes derived from Cyclo-octa-1,5-diene and Penta-1,3-Diene. Crystal and Molecular Structure of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ *

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In boiling octane, cyclo-octa-1,5-diene and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ react to give the compounds $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ and $[Mo(CO)_2(\eta^3\text{-}C_8H_{13})(\eta\text{-}C_5H_5)]$. An *X*-ray diffraction study has been carried out on the dimolybdenum species, crystals of which are monoclinic, a = 16.852(10), b = 7.427(2), c = 17.810(12) Å, β = 124.94(4)°, space group $P2_1/c$ (no. 14). The structure was solved by heavy-atom methods and has been refined to R 0.061 (R' 0.059) for 3 613 independent reflections. The alkyne group of a cyclo-oct-1-en-5-yne ligand forms a symmetrical transverse bridge across a Mo–Mo single bond [2.986(1) Å], with the ring adopting a ' tub ' conformation, concave to the metal–metal bond. This allows the alkene group to form a second ring-to-metal attachment involving only one of the metal atoms. This metal atom also carries one cyclopentadienyl group and one terminal carbonyl ligand. The other metal atom carries one cyclopentadienyl group and two carbonyl ligands, one of which, however, shows the characteristic geometry of a ' weakly semibridging ' carbonyl (Mo–C 1.94 and 2.89 Å, Mo–Mo–C 68°, Mo–C–O 170°). The molecule possesses no symmetry; the C_8 ring is twisted so that the alkene and alkyne moieties are not parallel to one another, and the other ligands are not symmetrically related to the metal–metal bond. The i.r. spectrum of the compound in solution indicates the existence of isomers. However, the ^1H and ^{13}C n.m.r. spectra are invariant down to −80 °C and therefore the isomers are interconverting sufficiently rapidly to provide averaged nuclear environments on the n.m.r. time-scale, although the nature of the spectra reveal the species present to lack symmetry. It is proposed that rotamers exist, produced by rotation of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ group about an axis through the midpoint of the μ-alkyne bond, with low barriers to their interconversion. The compound $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ reacts with CO to give $[Mo_2(CO)_4(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$, which shows dynamic n.m.r. properties similar to other $[Mo_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$ species. Treatment of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with buta-1,3-diene, 2-methylbuta-1,3-diene or 2,3-dimethylbuta-1,3-diene in boiling heptane or octane failed to give isolable dimolybdenum compounds, but a *cis/trans* mixture of penta-1,3-diene afforded the complex $[Mo_2(CO)_2(\mu\text{-}C_5H_8)(\eta\text{-}C_5H_5)_2]$, from the ^1H n.m.r. spectrum of which it is deduced that the $\mu\text{-}C_5H_8$ ligand is *cis*-MeCH=CH–CH=CH_2.

In the preceding paper [1] we described the chemistry of complexes derived from the reaction of cyclo-octatetraene with $[Mo_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 4 or 6). We now report on the related reactions of cyclo-octa-1,5-diene and penta-1,3-diene.

RESULTS AND DISCUSSION

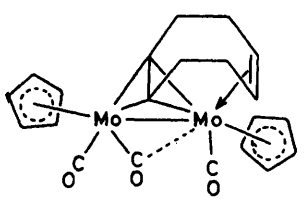
Reaction with Cyclo-octa-1,5-diene.—The reaction of cyclo-octa-1,5-diene with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ proceeds slowly in boiling octane to give a mixture of products. Two only of these were isolated in appreciable yield, the orange crystalline dimolybdenum complex $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1) and yellow crystalline $[Mo(CO)_2(\eta^3\text{-}C_8H_{13})(\eta\text{-}C_5H_5)]$ (2). The latter was identified as a cyclic η^3-allyl complex on the basis of its ^1H and ^{13}C n.m.r. spectra, once the mass spectrum and i.r. spectrum (carbonyl region) had shown it to be a mononuclear molybdenum dicarbonyl species.

The ^1H n.m.r. spectrum of (2) displays signals due to the η^3-allyl fragment at τ 5.85 (t, 1 H, J 8 Hz) and 6.25 (2 H), the latter resonance being subject to coupling to adjacent methylenic protons. Aliphatic proton resonances are observed at τ 7.76 (m, 3 H) and 8.54 (m, 7 H). Clear evidence of mirror symmetry in the C_8 ligand is provided by the ^{13}C n.m.r. spectrum, which shows five carbon resonances. Two of these are at typically sp^2 carbon shifts (δ 68.1 and 56.7 p.p.m.) and three at sp^3 carbon shifts (δ 32.9, 29.2, and 23.9 p.p.m.). The formation of the $\eta^3\text{-}C_8H_{13}$ ligand from cyclo-octa-1,5-diene may be seen against a background of varied hydrogenation, dehydrogenation, and rearrangement undergone by this diene in reactions with transition-metal carbonyls.[2-6]

The more interesting product of the reaction is $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1). We believe that, like the reaction of cyclo-octatetraene with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, the active metal species is $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, containing a metal–metal triple bond, and that a related mechanism is in operation.[1] The complexes are clearly similar in having a bridging cyclic alkyne ligand and additional co-ordination of olefinic bonds to one molybdenum. However, whereas cyclo-octatetraene has experienced hydrogen transfer to give the C_8H_8 ligand in (3),[1] cyclo-octa-1,5-diene has suffered loss of two hydrogen atoms in giving the C_8H_{10} ligand in (1). A related cyclo-oct-1-en-5-yne ligand has been observed previously, in the tetraruthenium complex $[Ru_4(CO)_{11}(\mu\text{-}C_8H_{10})]$ (4), formed through reaction of $[Ru_4H_4(CO)_{12}]$ with cyclo-octa-1,5-diene.[4]

The i.r. spectrum of (1) displays seven carbonyl stretching absorptions, indicating the existence in solution of probably three isomers. However, the ^1H n.m.r. spectrum has only two cyclopentadienyl proton resonances and three complex multiplets for the C_8H_{10} group, consistent with a single isomer. The same is true

* 1,1,2-Tricarbonyl-μ-[1′—2′-η-cyclo-oct-1′-en-5′-yne-$C^{5',6'}$-(Mo^1)$C^{5',6'}$(Mo^2)$C^{1'-2'}$(Mo^2)]-1,2-bis(η-cyclopentadienyl)dimolybdenum(*Mo–Mo*).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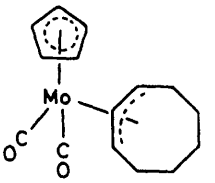
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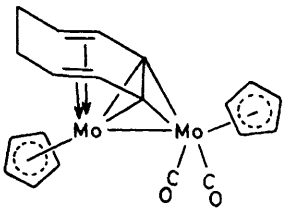
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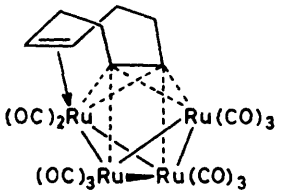
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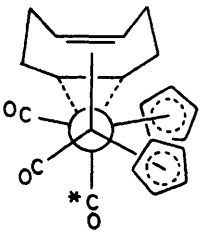
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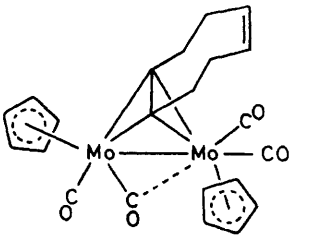
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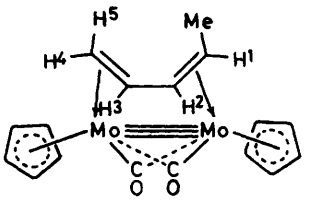
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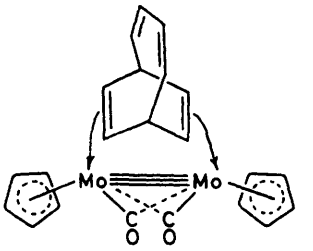
(8)

of the ^{13}C n.m.r. spectrum, which shows, in addition to two C_5H_5 signals, eight ring-carbon resonances. Two of these, at δ 93.9 and 88.3 p.p.m., are of low intensity, as expected for the μ-alkyne carbons which do not bear protons. The presence of eight C_8-ring resonances reveals the lack of symmetry in the molecule, a feature also manifested in the observation of three carbonyl carbon signals. Over a wide temperature range the ^1H (−85 to +110 °C) and ^{13}C (−80 to 0 °C) n.m.r. spectra of (1) are invariant, and it is therefore apparent that the isomers detected by i.r. are interconverting sufficiently rapidly to provide averaged nuclear environments on the n.m.r. time-scale. Moreover, in order to achieve a time-averaged structure with no symmetry each of the isomers must be asymmetric, and no exchange of nuclear environment can occur. In order to clarify this behaviour the molecular structure of (1) in the solid state was determined by *X*-ray diffraction.

The molecular structure of (1) is illustrated in Figure 1, which also shows the crystallographic numbering scheme. Atomic co-ordinates are listed in Table 1, bond lengths and interbond angles in Table 2; some least-squares planes and torsion angles are given in Table 3. The C_8 ring adopts a twisted ' tub ' conformation in which two opposite bonds, C(15)–C(16) and C(11)–C(12), are π-bonded to the $Mo_2(CO)_3(\eta\text{-}C_5H_5)_2$ framework of the molecule. As expected, C(15)–C(16) forms a symmetrical acetylenic transverse bridge across the Mo(1)–Mo(2) bond, while C(11)–C(12) forms an ethylenic attachment to Mo(2) only. The Mo(1)–Mo(2)–C_8 portion of the molecule does not have mirror symmetry because of the

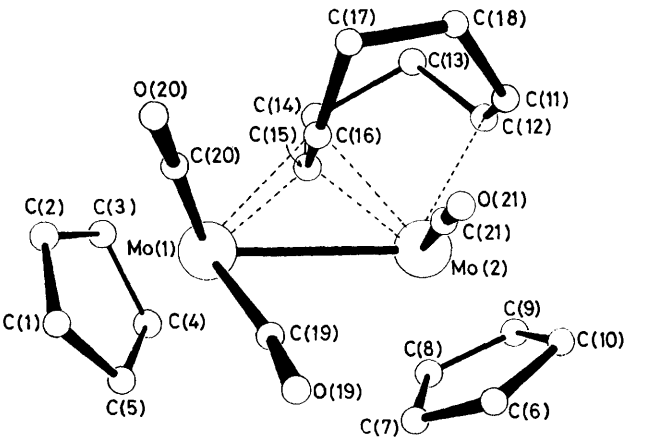

FIGURE 1 Molecular structure of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1), showing the crystallographic numbering sequence

twists in the C_8 ring; these can be clearly seen from the stereopair of Figure 2, or quantitatively from Table 3. This asymmetry is even more apparent in the rest of the molecule; the two cyclopentadienyl rings are not

equivalently related to the Mo–Mo bond, the two terminal carbonyl ligands are not coplanar, and the third carbonyl [which could perhaps be described as semi-bridging: Mo(1)–C(19) 1.94, Mo(2)–C(19) 2.89 Å and Mo(1)–C(19)–O(19) 169.6(6)°] makes an acute angle with the metal–metal bond [Mo(2)–Mo(1)–C(19) 68.1(2)°]. This is illustrated in Figure 3, which shows the molecule

TABLE 1

Atomic positional co-ordinates (fractional cell co-ordinates) for $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	0.171 8(10)	0.056 9(12)	−0.315 5(6)
C(2)	0.263 3(7)	−0.024 5(15)	−0.270 8(6)
C(3)	0.260 8(9)	−0.175 4(12)	−0.228 5(6)
C(4)	0.170 4(10)	−0.188 5(13)	−0.246 4(7)
C(5)	0.115 0(7)	−0.048 3(17)	−0.299 4(7)
C(6)	0.076 1(6)	0.076 6(11)	−0.033 2(7)
C(7)	0.062 7(6)	−0.021 3(13)	−0.104 4(6)
C(8)	0.106 4(6)	−0.193 3(12)	−0.069 2(7)
C(9)	0.143 8(6)	−0.196 2(10)	0.022 0(6)
C(10)	0.128 6(6)	−0.026 0(12)	0.046 9(6)
C(11)	0.375 1(5)	0.048 0(10)	0.151 9(4)
C(12)	0.359 0(5)	−0.133 2(10)	0.125 2(4)
C(13)	0.420 2(5)	−0.237 6(10)	0.103 1(5)
C(14)	0.369 4(5)	−0.255 0(8)	−0.000 9(5)
C(15)	0.319 8(5)	−0.079 5(8)	−0.036 2(4)
C(16)	0.350 2(5)	0.093 7(8)	−0.010 7(4)
C(17)	0.444 8(5)	0.174 9(11)	0.065 0(5)
C(18)	0.452 7(6)	0.163 8(11)	0.156 3(5)
C(19)	0.152 5(5)	0.248 4(10)	−0.161 8(5)
C(20)	0.324 5(6)	0.284 3(8)	−0.134 9(5)
C(21)	0.257 0(6)	0.283 5(9)	0.033 1(5)
Mo(1)	0.241 62(4)	0.079 34(7)	−0.159 46(3)
Mo(2)	0.230 61(4)	0.030 97(6)	0.000 82(3)
O(19)	0.096 8(5)	0.361 9(8)	−0.175 0(4)
O(20)	0.375 3(5)	0.401 2(8)	−0.121 9(5)
O(21)	0.271 0(5)	0.434 3(6)	0.052 5(5)

looking along the Mo–Mo bond. The ligands on Mo(2) are presumably constrained in their orientation by the bond C(11)–C(12) of the C_8 ring and the metal atom (although of course it could be argued, conversely, that the twist in the C_8 ring is a consequence of steric restraints within the crystal on the carbonyl and the cyclopentadienyl ligands). The two bonds between the ring and Mo(2) (taking the bond direction as the line joining the metal atom to the midpoint of the ring bond) are both approximately orthogonal to the Mo(2)–C(21)–O(21) direction (Table 2) although the angle subtended by the two ring bonds at Mo(2) is only *ca.* 75°. The ligands on Mo(1) are not subjected to the same restriction as those on Mo(2). The two carbonyl ligands are nearly orthogonal to one another, and the plane containing these two ligands is approximately orthogonal to the Mo(1)–C(15,16) direction: a fact which is of some importance in relation to the easy rotation of the Mo(1)$(\eta\text{-}C_5H_5)(CO)_2$ group around this direction (see below). The Mo–Mo distance of 2.986(1) Å is characteristic of a single bond, as is also required by the electron count. Figure 4 shows the packing of the molecules in the monoclinic (pseudo-hexagonal) unit cell.

The lack of symmetry characteristic of (1) in the solid state must, as discussed earlier, also apply to each of the isomers present in solution. The presence of one or more species containing exclusively terminal carbonyl groups is indicated by the i.r. spectrum, whose seven bands include only one typical of a semi-bridging CO, such as is present in the solid state. The solid-state

TABLE 2

Bond distances (Å) and angles (°) for $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1)

(*a*) Distances

Mo and cyclo-oct-1-en-5-yne			
Mo(1)–Mo(2)	2.986(1)		
Mo(1)–C(15)	2.153(6)	C(11)–C(12)	1.401(10)
Mo(1)–C(16)	2.197(6)	C(12)–C(13)	1.512(10)
		C(13)–C(14)	1.536(10)
Mo(2)–C(15)	2.113(6)	C(14)–C(15)	1.484(8)
Mo(2)–C(16)	2.189(7)	C(15)–C(16)	1.364(8)
		C(16)–C(17)	1.499(9)
Mo(2)–C(11)	2.383(7)	C(17)–C(18)	1.551(10)
Mo(2)–C(12)	2.363(6)	C(18)–C(11)	1.529(11)
Carbonyl groups			
Mo(1)–C(19)	1.940(7)	C(19)–O(19)	1.180(8)
Mo(2)–C(19)	2.891(7)		
Mo(1)–C(20)	1.939(7)	C(20)–O(20)	1.146(9)
Mo(2)–C(21)	1.937(7)	C(21)–O(21)	1.156(8)
Cyclopentadienyl rings			
Mo(1)–C(1)	2.321(8)	C(1)–C(2)	1.404(15)
Mo(1)–C(2)	2.344(8)	C(2)–C(3)	1.365(14)
Mo(1)–C(3)	2.377(8)	C(3)–C(4)	1.369(15)
Mo(1)–C(4)	2.380(8)	C(4)–C(5)	1.355(16)
Mo(1)–C(5)	2.360(8)	C(5)–C(1)	1.386(16)
Mo(2)–C(6)	2.336(8)	C(6)–C(7)	1.364(18)
Mo(2)–C(7)	2.365(8)	C(7)–C(8)	1.428(18)
Mo(2)–C(8)	2.392(7)	C(8)–C(9)	1.366(13)
Mo(2)–C(9)	2.400(7)	C(9)–C(10)	1.411(12)
Mo(2)–C(10)	2.329(8)	C(10)–C(6)	1.398(12)

(*b*) Angles

Cyclo-oct-1-en-5-yne			
C(18)–C(11)–C(12)	123.5(7)	C(14)–C(15)–C(16)	132.2(6)
C(11)–C(12)–C(13)	123.5(7)	C(15)–C(16)–C(17)	133.2(6)
C(12)–C(13)–C(14)	111.4(5)	C(16)–C(17)–C(18)	109.6(6)
C(13)–C(14)–C(15)	103.0(5)	C(17)–C(18)–C(11)	114.5(6)
Carbonyl groups			
Mo(1)–C(19)–O(19)	169.6(6)	Mo(2)–C(21)–O(21)	178.5(7)
Mo(1)–C(20)–O(20)	177.0(6)		
About Mo atoms			
Mo(2)–Mo(1)–C(19)	68.1(2)	C(19)–Mo(1)–C(20)	86.9(3)
Mo(2)–Mo(1)–C(20)	108.1(2)		
C(11,12)–Mo(2)–C(15,16) *	74.6		
C(11,12)–Mo(2)–C(21)	89.7		
C(21)–Mo(2)–C(15,16)	96.7		

* C(11,12) is the midpoint of C(11)–C(12) and C(15,16) is the midpoint of C(15)–C(16).

structure may be represented approximately by (5), where the molecule is viewed along the Mo–Mo axis from Mo(2) towards Mo(1), with the semi-bridging CO indicated by an asterisk. In solution it is likely that the ligands on Mo(2) will remain fixed in position, because of the co-ordination of an olefinic bond of the C_8 ring, but this is not necessarily so for Mo(1). Rotation of the ligands on Mo(1), perhaps about an axis through the midpoint of the μ-alkyne bond [C(15)–C(16) of Figure 1], will bring the semi-bridging CO out of this role and create new isomers with only terminal carbonyl groups. It is to the existence of such rotamers, with low barriers to their interconversion, that we attribute the unusual

spectroscopic behaviour of (1). The dynamic stereochemistry of complexes $[Mo_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$, of which class compound (1) may be considered a special member, has been investigated and proposed to involve similar rotational interconversions.[7]

The relationship of (1) to this class of μ-alkyne complexes was illustrated by subjecting (1) to 200 atm * of CO at 60 °C. Under these conditions a good yield of the black crystalline compound $[Mo_2(CO)_4(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (6) was obtained. The spectroscopic properties of

TABLE 3

Equations of some least-squares planes and lines * for complex (1), with distances (Å) of the relevant atoms from planes in square brackets

Plane (1): C(18), C(11), C(12), C(13)
$1.806x + 1.896y + 12.936z = 2.536$
[C(18) −0.007, C(11) 0.015, C(12) −0.015, C(13) 0.007]
Plane (2): C(12), C(13), C(14), C(15)
$12.101x + 4.641y - 2.854z = 3.486$
[C(12) −0.118, C(13) 0.202, C(14) −0.197, C(15) 0.112]
Plane (3): C(14), C(15), C(16), C(17)
$-13.270x - 0.272y + 17.014z = -4.843$
[C(14) −0.005, C(15) 0.012, C(16) −0.012, C(17) 0.005]
Plane (4): C(16), C(17), C(18), C(11)
$-8.474x + 6.299y + 2.698z = -2.436$
[C(16) 0.030, C(17) −0.052, C(18) 0.053, C(11) −0.030]
Plane (5): C(1), C(2), C(3), C(4), C(5)
$-3.340x + 3.973y + 14.013z = -4.770$
[Mo(1) 2.044]
Plane (6): C(6), C(7), C(8), C(9), C(10)
$15.495x + 2.542y - 6.562z = 1.602$
[Mo(2) 2.045]
Line (7): Mo(1), Mo(2)
$l = -0.609\,8$, $m = -0.120\,3$, $n = 0.991\,4$
Line (8): C(11), C(12)
$l = -0.008\,3$, $m = -0.961\,1$, $n = -0.221\,5$
Line (9): C(15), C(16)
$l = 0.188\,6$, $m = 0.942\,8$, $n = 0.117\,5$

Angles (°) between planes and lines

(1)–(3)	58.9	(7)–(8)	95.5
(2)–(4)	83.2	(7)–(9)	90.7
(5)–(7)	44.4	(8)–(9)	10.4
(6)–(7)	26.8		

Torsion angles around the C_8 ring

C(18)–C(11)–C(12)–C(13)	2.9
C(11)–C(12)–C(13)–C(14)	−101.7
C(12)–C(13)–C(14)–C(15)	36.8
C(13)–C(14)–C(15)–C(16)	48.9
C(14)–C(15)–C(16)–C(17)	−3.9
C(15)–C(16)–C(17)–C(18)	−78.1
C(16)–C(17)–C(18)–C(11)	9.9
C(17)–C(18)–C(11)–C(12)	57.1

* x, y, z are fractional co-ordinates; l, m, n are the direction cosines with a, b, c respectively.

(6) are as expected for a μ-alkyne complex of the $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$ unit. Thus, the i.r. spectrum shows the presence of both terminal and semi-bridging [ν(CO) 1 845 cm^{-1}] carbonyl groups, while the ^1H n.m.r. spectrum reveals apparently mirror symmetry for the molecule, having a single cyclopentadienyl ring signal at τ 4.80 and three signals for C_8H_{10} ring protons [at τ 4.34 (m, 2 H), 6.81 (m, 4 H), and 7.73 (m, 4 H)]. This symmetry undoubtedly arises from stereochemical non-rigidity of (6), of the type referred to above for $[Mo_2(CO)_4(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2]$ complexes in general. Studies with a variety of such species have revealed that there is in operation a low-energy carbonyl exchange process which generates C_2 symmetry and a higher energy process which produces C_{2v} symmetry overall.[7] The effect for a symmetrically substituted alkyne is to generate one time-averaged CO environment at the high-temperature limit. At −95 °C, in CD_2Cl_2, (6) has two CO signals in its ^{13}C n.m.r. spectrum, at δ 233.6 and 230.9 p.p.m. These broaden on warming and coalescence at *ca.* −70 °C, before developing into a sharp singlet (231.9 p.p.m.) above −40 °C. Clearly, the lower energy process is occurring rapidly even at −95 °C, effecting pair-wise averaging of CO groups, but by −40 °C total averaging is achieved through the onset of the second process. In a subsequent paper we will describe studies which shed considerable light on the nature of these processes.[8] In so doing, the presence of weak carbonyl bands in the i.r. spectrum of (6) will be explained.

* Throughout this paper: 1 atm = 101 325 N m^{-2}.

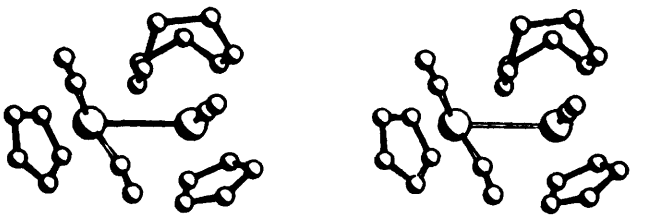

FIGURE 2 Stereoscopic view of the structure of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1)

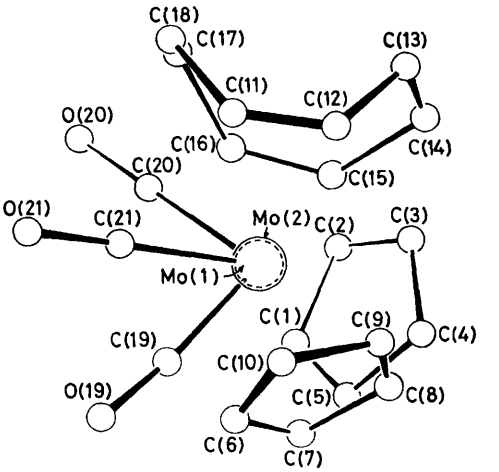

FIGURE 3 View of the molecule along the Mo–Mo bond from Mo(2) to Mo(1), showing the relative disposition of the ligands around the two metal atoms

Reactions with 1,3-*Dienes*.—In this paper, and in the immediately preceding one,[1] it has been shown that $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ {reacting as $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in a boiling hydrocarbon} yields complexes derived from cyclic polyolefins. It was therefore of interest to determine whether the dimolybdenum cyclopentadienyl carbonyls are reactive towards acyclic polyolefins, especially in view of the apparent unreactivity of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with mono-olefins.[9,10] Treatment of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with buta-1,3-diene, 2-methylbuta-1,3-diene, and 2,3-dimethylbuta-1,3-diene in boiling

heptane or octane did result in reactions, but no dimetallic species were produced. Only uncharacterised yellow oils were obtained. However, the reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with a mixture of *cis*- and *trans*-penta-1,3-diene under the same conditions led to the isolation of a black crystalline complex in low yield. On the basis of i.r., ^1H n.m.r., and mass spectra, and

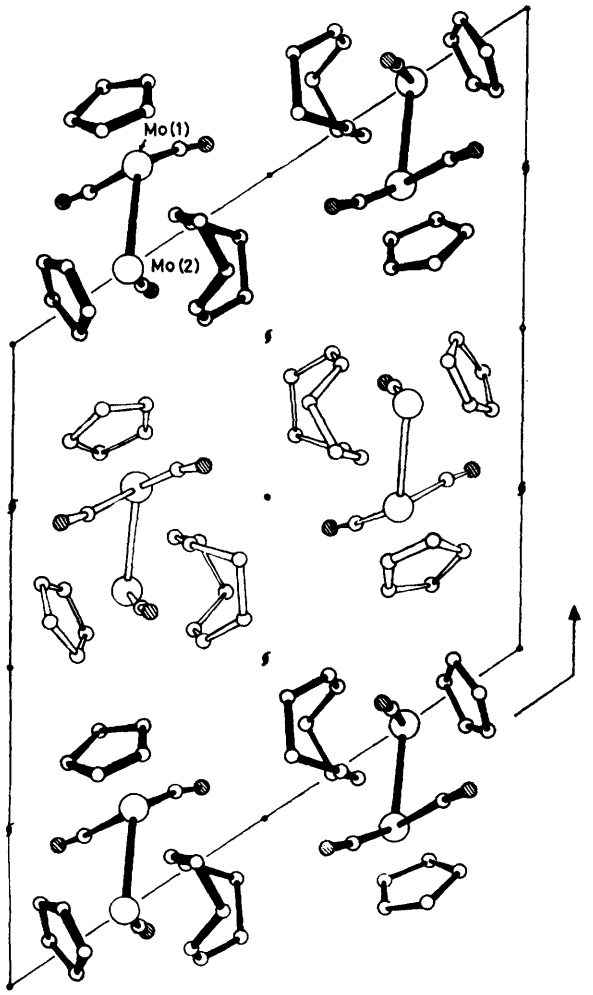

FIGURE 4 Packing of the molecules of (1) in the monoclinic (pseudohexagonal) unit cell. Atoms Mo(2) form an array which has nearly hexagonal symmetry

elemental analyses, this species was identified as $[Mo_2(CO)_2(\mu\text{-}C_5H_8)(\eta\text{-}C_5H_5)_2]$ (7), crystallising with 0.5 mol of dichloromethane. The latter is evident in the ^1H n.m.r. spectrum, as are two inequivalent cyclopentadienyl ligands and signals attributable to a molecule of penta-1,3-diene bridging two molybdenum atoms, as indicated. The size and pattern of coupling between the protons of the bridging ligand allows unequivocal assignment of the n.m.r. spectrum as given in the Experimental section. The coupling between H^1 and H^2 and between H^2 and H^3 is 7 Hz in each case, typical of a *cis* orientation of protons on an olefinic bond. This therefore indicates that the diene bonds to the dimolybdenum unit as illustrated, and is the *cis*-penta-1,3-diene isomer in co-ordination.

The ' 18-electron rule ' requires the presence of a triple Mo–Mo bond in (7). From the i.r. spectrum, which has carbonyl bands at 1 818 and 1 799 cm^{-1}, the metal–metal bonding is evidently supported by two bridging carbonyl groups. By comparison with $[Mo_2(CO)_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$ (8),[11] whose structure has been determined by *X*-ray diffraction and whose semi-bridging CO groups are seen at 1 805 cm^{-1} in the i.r. spectrum, those in (7) are similarly semi-bridging. The structures of (7) and (8) are obviously closely related.

Although co-ordination of 1,3-dienes to a single metal is common, bonding with a multinuclear metal system is very rare. Previously it has been observed[12] that 1,3-dienes form adducts with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in solution, perhaps involving diene bridging, and very recently the cluster $[Ru_6C(CO)_{15}(\mu\text{-}MeCH{=}CH{-}CH{=}CHMe)]$ has been shown to have *trans,trans*-hexa-2,4-diene spanning one edge of an Ru_6 octahedron.[13]

In conclusion, although it appears that the triple bond in $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is unreactive towards mono-olefins, excluding 3,3-dimethylcyclopropene,[14] *it* is reactive towards allene,[9] acyclic 1,3-dienes, and cyclic polyolefins. The consequences of reaction are varied. Only allene and *cis*-penta-1,3-diene co-ordinate unchanged at the dimetal centre, while 2,3-dimethylcyclopropene undergoes ring-opening. Cyclo-octatetraene and cyclo-octa-1,5-diene retain their rings, but the former rearranges and the latter loses two hydrogen atoms.

EXPERIMENTAL

Instrumentation and techniques were as described earlier.[1] Infrared spectra were measured in hexane, and n.m.r. spectra in $CDCl_3$, unless otherwise stated.

Reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ *with Cyclo-octa-1,5-diene.*—A mixture of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (5 g, 10.2 mmol) and cyclo-octa-1,5-diene (12 g, 111 mmol) was heated at reflux in octane (200 cm^3) for 14 d. The brown solution was chromatographed on alumina, elution with hexane affording several yellow bands. All but the last of these were discarded because they contained little material. The last gave 0.66 g (10%) of yellow *crystals* of $[Mo(CO)_2(\eta^3\text{-}C_8H_{13})(\eta\text{-}C_5H_5)_2]$ (2), m.p. 115—116 °C; $\nu_{max.}$ (CO) 1 949s and 1 876s cm^{-1}; ^1H n.m.r., τ 4.78 (s, 5 H), 5.85 (t, 1 H, *J* 8 Hz), 6.25 (m, 2 H), 7.76 (m, 3 H), 8.54 (m, 7 H); ^{13}C n.m.r., δ(p.p.m.) 238.8 (CO), 91.7 (C_5H_5), 68.1 (CH), 56.7 (CH), 32.9 (CH_2), 29.2 (CH_2), 23.9 (CH_2) (Found: C, 55.4; H, 5.5; *M* 328. $C_{15}H_{18}MoO_2$ requires C, 55.2; H, 5.5%; *M* 328), after crystallisation from hexane–dichloromethane. Further elution with dichloromethane–hexane (2 : 3) developed an orange band which provided 0.43 g (8%) of orange needle-like *crystals* of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1), m.p. 136—138 °C (decomp.); $\nu_{max.}$ (CO) 1 966s, 1 951s, 1 938w, 1 922s, 1 906s, 1 897s, and 1 842m cm^{-1}; ^1H n.m.r. (CD_2Cl_2 at −78 °C), τ 4.64 (s, 5 H), 4.94 (s, 5 H), 6.30 (m, 4 H), 7.46 (m, 5 H), and 8.15 (m, 1 H); ^{13}C n.m.r. (CD_2Cl_2 at −78 °C), δ(p.p.m.) 239.3 (CO), 232.5 (CO), 232.1 (CO), 93.9 (C), 92.7 (C_5H_5), 91.0 (C_5H_5), 88.3 (C), 73.0 (CH), 70.9 (CH), 48.1 (CH_2), 32.8 (CH_2), 30.4 (CH_2), 30.0 (CH_2)

(Found: C, 49.1; H, 4.0; *M* 512. $C_{21}H_{20}Mo_2O_3$ requires C, 49.2; H, 4.0%; *M* 512) upon crystallisation from hexane–dichloromethane.

Carbonylation of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1).—A hexane (50 cm³) solution of (1) (120 mg, 0.23 mmol) was heated at 60 °C in an autoclave charged to 200 atm of CO for 18 h. Chromatography of the reaction mixture, eluting with dichloromethane–hexane (1 : 6), provided a trace of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ followed by a maroon band which gave 72 mg (65%) of dark maroon *crystals* of $[Mo_2(CO)_4(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (6), m.p. 107 °C (decomp.); $\nu_{max.}$ (CO) 1 980m, 1 947w, 1 919s, 1 912s, 1 893w, 1 845w, and 1 838 (sh) cm⁻¹; ^{1}H n.m.r., τ 4.34 (m, 2 H, CH), 4.80 (s, 10 H, C_5H_5), 6.81 (m, 4 H, CH_2), 7.73 (m, 4 H, CH_2); ^{13}C n.m.r., δ(p.p.m.) 231.5 (CO), 130.4 (CH), 92.1 (C_5H_5), 88.5 (C), 39.3 (CH_2), 28.2 (CH_2) (Found: C, 48.9; H, 3.7; *M* 540. $C_{22}H_{20}Mo_2O_4$ requires C, 48.9; H, 4.1%; *M* 540).

Reaction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ *with Penta-1,3-diene*.—A mixture of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (1 g, 2.04 mmol) and penta-1,3-diene (*cis* and *trans* isomers) (4 g, 59 mmol) was heated in heptane (150 cm³) at reflux for 21 d, to give a yellow-brown solution with much insoluble solid in suspension. Evaporation of solvent, followed by chromatography of soluble material, afforded, on elution with hexane, a yellow air-sensitive oil which was not identified. Further elution with dichloromethane developed a brown band which, after crystallisation from dichloromethane–hexane, yielded 17 mg (2%) of brown *crystals* of $[Mo_2(CO)_2(\mu\text{-}C_5H_8)(\eta\text{-}C_5H_5)_2]\cdot 0.5CH_2Cl_2$ (7), m.p. 130 °C (decomp.); $\nu_{max.}$ (CO) 1 818m and 1 799s cm⁻¹; ^{1}H n.m.r., τ 4.70 (s, 1 H, CH_2Cl_2), 5.03 (s, 5 H, C_5H_5), 5.07 (s, 5 H, C_5H_5), 5.96 [d of t, H^3, $J(H^2H^3)$ 7, $J(H^3H^4)$ 7, $J(H^3H^5)$ 10], 6.34 [quin, H^1, $J(H^1H^2)$ 7, $J(MeH^1)$ 7], 7.21 [t, H^2, $J(H^1H^2)$ 7, $J(H^2H^3)$ 7], 7.55 [d of d, H^4, $J(H^3H^4)$ 7, $J(H^4H^5)$ 2], 7.83 [d of d, H^5, $J(H^3H^5)$ 10, $J(H^4H^5)$ 2], 8.23 [d, Me, $J(MeH^1)$ 7 Hz] [Found: C, 43.0; H, 4.8; *M* 446. $C_{17.5}ClH_{19}Mo_2O_2$ requires C, 43.0; H, 3.9%; *M* 446 (for molybdenum complex only)].

Crystal Structure Determination of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$ (1).—Crystals of (1) grow as orange needles from dichloromethane–hexane. Intensities were measured at room temperature from a crystal of dimensions 0.50 × 0.25 × 0.05 mm in the range $2.9 \leqslant 2\theta \leqslant 55°$, using a variable scan rate of between 0.488° s⁻¹ and 0.048 8° s⁻¹, according to the magnitude of a 2-s pre-scan count, the extreme scan rates corresponding to 1 500 and 150 counts, respectively. Three standard reflections were remeasured every 40 reflections; these showed only random fluctuations over 172 h of crystal exposure to *X*-rays. The structure was solved and refined from 3 613 independent intensities for which $I \geqslant 1.0\sigma(I)$, derived from a total of 6 260 after merging equivalent reflections of the type *hkl* and *hk̄l*. No correction was made for the effects of *X*-ray absorption [μ(Mo-K_α) = 12.5 cm⁻¹].

Crystal data. $C_{21}H_{20}Mo_2O_3$, *M* = 512.2, Monoclinic, *a* = 16.852(10), *b* = 7.427(2), *c* = 17.810(12) Å, β = 124.94(4)°, *U* = 1 827(2) Å³, D_m(flotation) = 1.80 g cm⁻³, *Z* = 4, D_c = 1.86 g cm⁻³, *F*(000) = 1 016, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator) λ = 0.710 69 Å, μ(Mo-K_α) = 12.5 cm⁻¹.

Structure solution and refinement. The molybdenum atoms were located from a sharpened Patterson synthesis. The location of one of these, Mo(2), at *x* = 0.23, *y* = 0.03, and *z* = 0.00, coupled with lattice parameters of *a* = 16.8, *c* = 17.8, and an interaxial angle close to 120° (β = 125°), confers on the structure a strong pseudo-hexagonal symmetry. Difficulties were therefore experienced both in locating the lighter atoms and in refining the structure with anisotropic thermal motion for all non-hydrogen atoms. The first problem was overcome by proceeding slowly and carefully with electron-density difference syntheses, and by keeping the cyclopentadienyl rings, once located, as rigid groups until a complete solution was obtained. The C atoms were then allowed to refine individually. The second problem was more intractable. If no constraints were applied, correlation coefficients of between 0.50 and 0.75 were obtained, for any one atom, between *x* and *z*, U_{11} and U_{13}, U_{33} and U_{31}, U_{23} and U_{12}. On the other hand, if constraints appropriate to true hexagonal symmetry were applied for the thermal parameters ($U_{11} = U_{33}$, U_{22} independent, $U_{23} = U_{12} = 0$, and $U_{13} = \frac{1}{2}U_{11}$) and then refinement was allowed, first fixing *x* and refining *y* and *z*, then fixing *z* and refining *x* and *y*, no better overall result was obtained. The residuals and e.s.d.s of the parameters were all higher than if the pseudo-symmetry had been completely ignored. Neither method is ideal; the one assumes that the offending correlation coefficients are small, the other, that they are unity. The results listed in this paper are those obtained from free refinements, during which optimised weights were used according to the scheme $w = 1.251\,[\sigma^2(F_o) + 0.001\,4|F_o|^2]^{-1}$. Hydrogen atoms were incorporated at calculated positions (C–H = 0.95 Å; $U_{iso.}$ = 0.05 Å²). Residual electron densities of between +1.5 and −2.3 e Å⁻³ were found, particularly in the neighbourhood of the metal atoms, and were doubtless a reflection of initially poor quality data combined with pseudo-symmetry problems. The refinement converged at *R* 0.061 (*R'* 0.059). Atomic scattering factors were those of ref. 15 for all non-hydrogen atoms, and those of ref. 16 for hydrogen. All computational work was carried out on the South-Western Universities Network with the SHELX system of programs.[17] Observed and calculated structure factors, all thermal parameters, and hydrogen-atom co-ordinates are listed in Supplementary Publication No. SUP 23141 (28 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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